
CLAIMS

[Claim(s)]
[Claim 1] The manufacture approach of the fullerene which is made to generate thermal plasma, supply a carbon-containing compound raw material into this, are heating and the manufacture approach of fullerene of carrying out a decomposition reaction, cooling this reactant gas, collecting solid content, and separating fullerene from this recovery object, about this, and are characterized by having gone caudad and having arranged the generating section, the reaction section, and the stripping section of thermal plasma from the upper part.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the approach of manufacturing fullerene efficiently.
[0002]
[Description of the Prior Art] Fullerene is the spherical carbon allotropes of the numbers of high carbon, such as C60 and C70. C60 has the molecular structure of the football of truncated forward 20 face piece.
[0003] The approach of cooling the carbon gas which the graphite was evaporated in the manufacture approach of the conventional fullerene (for example, evaporation by the evaporation by laser radiation, the evaporation by the resistance heating of high current density, arc discharge generating between graphite electrodes, etc.), and generated it to it is learned.
[0004] As another conventional method of the manufacture approach of fullerene, benzene / O2 / Ar premixing gas is burned under low voltage, and there is the approach of cooling the generated gas.
[0005]
[Problem(s) to be Solved by the Invention] A conductive solid-state graphite (evaporation heat of decomposition is large and evaporation temperature is high.) must be used for the manufacture approach of the former fullerene, and there is a problem that a vapor rate is low and energy efficiency is low (less than 1%) in it. Moreover, continuous feeding also has the problem of being difficult.
[0006] In the manufacture approach of the latter fullerene, the control width of face of temperature conditions is restricted to a stationary burning temperature requirement, and since combustion attainment temperature is about 1800K, the perfect pyrolysis of a raw material is difficult. Moreover, it is O2 beyond the need. When it supplies, the amount of raw materials lost by combustion increases, there is also a possibility of understanding the fullerene generated further an oxidized part, and it is O2 [required for heating (stationary burning)]. There is a problem that balance and optimization with an amount are difficult.
[0007] Therefore, these approaches are unsuitable as a lot of manufacturing methods of fullerene.
[0008]
[Means for Solving the Problem] The manufacture approach of the fullerene of this invention generates thermal plasma, supplies a carbon-containing compound raw material into this, are heating and the manufacture approach of fullerene of carrying out a decomposition reaction, cooling this reactant gas, collecting solid content, and separating fullerene from this recovery object, about this, and is characterized by having gone caudad and having arranged the generating section, the reaction section, and the stripping section of thermal plasma from the upper part.
[0009] Hereafter, this invention is further explained to a detail.
[0010] In this invention, the approach of carrying out heating ionization of the plasma gas of a specific kind is desirable as an approach of generating thermal plasma. Specifically, a DC arc

discharge plasma jet type plasma gun device and 100kHz - about 10GHz RF induction thermal plasma developmental mechanics are illustrated.
[0011] In addition, DC arc discharge plasma jet developmental mechanics and RF induction thermal plasma developmental mechanics are used together, and you may make it generate thermal plasma. In this case, stable thermal plasma can be generated to change of a feeding rate covering the large volume, and fullerene can be compounded in large quantities at high speed.
[0012] As this plasma gas, it is helium, Ar or helium/H2, Ar/H2, helium/O2, Ar/O2, helium/Ar/H2, helium/Ar/O2, helium/Ar/H2 / O2. Or helium/Ar/H2 O is desirable. Heating ionization of this gas is carried out using a suitable means, and thermal plasma is generated. As for the highest attainment temperature of thermal plasma, 3500-15000K are preferably good more than 2000K.
[0013] It is desirable that it is the compound with which the whole contains carbon 65% or less by the atomic ratio as a carbon-containing compound raw material supplied into this thermal plasma. Generally, a perfect pyrolysis is comparatively easy for these also among carbon-containing compound raw materials, and since they are cheap raw materials, they can compound fullerene cheaply at high effectiveness.
[0014] Specifically, in the case of the organic substance, the following compounds are desirable as this raw material.
[0015] The aromatic compound and complex aromatic compounds of a monocycle, such as benzene, a pyridine, a cyclopentadiene, a pyrrole, a furan, and a thiophene, Or those methyls, hydroxy ** or a mel helmet substitution product, naphthalene, A quinoline, an indene, Indore, benzofuran, benzothiophene, An anthracene, an acridine, a phenanthrene, phenanthridine, a fluorene, A carbazole, a dibenzofuran, a dibenzo thiophene, an acenaphthylene, A condensed multi-ring aromatic compound and condensed multi-ring complex aromatic compounds, such as a pyrene and fluoranthene, Or those methyls, hydroxy ** or a mel helmet substitution product, a biphenyl, A polycyclic ring set aromatic compound and polycyclic ring set complex aromatic compounds, such as a 2 and 2'-(or 4 and 4'-) bipyridine and o-(or m- or p-) terphenyl, Or those methyls, hydroxy ** or a mel helmet substitution product, o-(or p-) benzoquinone, 1,4-naphthoquinone, 9,10-anthraquinone, and 9-full -- me -- aromatic ketone, such as non, and a quinone -- Or those methyls, hydroxy ** or a mel helmet substitution product, ethylene, Partial saturation aliphatic hydrocarbon, such as 1-butene, 1,3-butadiene, acetylene, 1-butyne, 1, and 3-Buta Jean, ** et al. [or] -- ** -- methyl and hydroxy ** or a mel helmet substitution product, and methane -- Saturated aliphatic hydrocarbon, such as ethane, a propane, n-(or ISO) butane, n-(or iso ****** neo) pentane, n-hexane, a cyclohexane, n-heptane, and n-octane, or those methyls, hydroxy **, or a mel helmet substitution product.
[0016] Moreover, in an inorganic substance, CS2, CO, etc. are desirable as this raw material. especially -- CS2 a case -- dehydrogenation indispensable in the case of the organic substance -- passing -- without -- very -- easy -- a pyrolysis -- it is carried out and fullerene can be compounded. H2 In composition of the fullerene by the plasma gas which is not contained, since there is no subgeneration of the organic substance in the case of an inorganic substance raw material, separation purification of the fullerene from a product is easy.
[0017] The above carbon-containing compound raw material is independent, or is used combining two or more sorts.
[0018] Once the raw material supplied into thermal plasma is preferably heated to 2500K or more more than 2000K, it radiates heat. It is made to make the temperature region of 2500-1300K stay at 1300K or more temperature regions for 10 to 100ms preferably for 1 to 500ms at this time.
[0019] In addition, as for the internal pressure of the plasma reaction section, maintaining at 10 - 300Torr is desirable. The carbon produced by decomposition in this thermal plasma carries out clustering, and fullerene generates. It is cooled and the products containing these fullerene are collected as solid content.
[0020] What is depended on natural radiationnal cooling or adiabatic expansion of plasma

gas/resultant as the cooling approach of gas including a resultant; it is low-temperature helium and N2. And the thing which depends either or the mixed inert gas (a liquefied gas is included), such as Ar, on adding to plasma gas/resultant; there are some which are depended on contact of heat exchange cooling, for example, the plasma gas/resultant to a water cooled furnace wall. Under the present circumstances, in order to prevent the outflow by denaturation and un-solidifying, 400 degrees C or less cool in the cooling section to about 100 degrees C or less preferably as quickly as possible. [which were generated] [of fullerene] It depends for the amount of exhaust heat required for cooling on plasma gas and a feeding rate, and the magnitude of the supply energy for plasma generating.

[0021] In this way, the product cooled and solidified is recovered by recovery means (for example, a recovery wall, a bag filter, etc.). When cooling by radiationnal cooling or heat exchange, it can also serve both as a cooling means and a recovery means.

[0022] By the way, if it faces cooling and solidifying a product and collecting these and is made to produce a soot-like product under a reduced pressure air current, there are many amounts which flow into exhaust air systems (vacuum pump etc.), without the ability collecting products, and the recovery effectiveness of a product cannot necessarily become high easily. Furthermore, since a product deposits on a vacuum pump etc., cooling effectiveness falls, therefore recovery of a continuous product becomes difficult.

[0023] In order to avoid this, in this invention, sequential installation of a plasma generating system, the reaction section, and the cooling system is carried out caudad toward length, and products are further transported and collected to the stripping section prepared caudad.

[0024] In this this invention approach, without being efficiently discharged by the effectiveness of both forced convections by the gas stream of free fall by gravity, and the cooled plasma gas, and piling up from a cooling system, according to it, to a downward stripping section, it is transported and the produced soot-like products are collected.

[0025] As this stripping section, the thing of the format of the shape of a container (a collection tank and cyclone), a bag filter, etc. is used. Moreover, you may make it collect the products which were not able to be collected in the first step by installing any these one under the cooling system, collecting most products once and installing above-mentioned one of one more or more recovery systems in the lower stream of a river further.

[0026] Moreover, in the above cooling and a recovery process, if the product accumulated on the surface of the cooling system, without being discharged from a cooling system and going out is operated making it **** at any time, products will be collected still more efficiently.

[0027] The thing of a configuration like the sweeper who fails to write a product from a cooling system front face as this desorption approach can be used. Moreover, inert gas (Ar, helium, N2, etc.) may be made to blow off from a nozzle, and a product may be desorbed compulsorily. In that case, it is good to make it blow off so that it may go caudad from the upper part and inert gas may be applied to a cooling system front face so that a product may be transported to the stripping section installed caudad.

[0028] The plasma gas after cooling may be used as this inert gas. Moreover, a recovery system may be excited and a product may be desorbed.

[0029] In order to collect products completely by the recovery system, the configuration of a recovery system is set that the rate of flow of the gas in a recovery system becomes 1 or less m/s preferably. In addition, in process of a plasma reaction, in many cases, the organic substance, soot, etc. arise as a by-product, and fullerene and such mixture are collected in this case. The separation method of the collected product has the reverse sublimation by re-cooling of reheating / volatilization gas of a product, the extract by the solvent with meltable fullerene, etc. These may be combined suitably and may be used.

[0030] In addition, especially when dissociating at an elevated temperature like [in an extract] using a solvent with a possibility of deteriorating fullerene etc., it is desirable to isolate completely and to operate the path which results in a plasma generating system, the plasma reaction section, a cooling system, and a recovery system, and this segregate from a feeding system. It is good to carry out, after even an airtight and the isolated extractor transport the

product from which you made it beforehand desorbed mechanically, and it was desorbed at this time. It is desirable to carry out, after making it **** mechanically first also in reverse sublimation and making it transport to an airtight and the isolated reverse sublimator.
[0031] When reverse sublimation separates fullerene, it is helium and N2. And volatilization gas is cooled and collected after heating to suitable temperature under either, such as Ar, or the ambient atmosphere of the mixed inert gas. In for example, 10-6Torr, about 500 degrees C or more and cooling temperature have [whenever / this stoving temperature] desirable 100 degrees C or less at about 400 degrees C or more and ordinary pressure.
[0032] Moreover, when an extract separates fullerene, it is desirable to use solvent [ten or less volatile solvent which dissolves well / without carrying out the chemical change of the generation fullerene as a solvent], for example, a carbon number, liquefied saturation or unsaturated hydrocarbon, benzene, toluene, CS2, a pyridine, etc.
[0033] As an extractor, a batch type extractor, for example, a Soxhlet extractor etc., can be used. At this time, an extract can also be sped up by heating, ultrasonic irradiation, etc. Fullerene is separated and collected from the soot of a by-product etc. by these approaches.
[0034] Then, if there is need, liquid chromatography or supercritical fluid chromatography will isolate and refine fullerene.
[0035] In the synthetic approach of the above fullerene, all the inside of the path from a feeding system to a plasma generating system, the plasma reaction section, a cooling system, and a recovery system is intercepted from the open air. What is necessary is just to install a part for the whole member of this path, or the principal part in the chamber 20 exhausted by the vacuum pump 19, as shown in Fig. 1st [the] and 4 in order to intercept with the open air. In addition, only the inside of this path may be constituted as the pipe line, and you may intercept from the open air.
[0036]
[Function] According to the manufacture approach of the fullerene of this invention, the continuation supply of the carbon-containing compound raw material of a gas, a liquid, or fine particles can be carried out. Moreover, since decomposition temperature is low and catabolic rate is large compared with a graphite, it can fully heat and decompose within the residence time in thermal plasma, and these raw materials can compound fullerene with sufficient energy efficiency quickly. It differs from the approach combustion furthermore performs heating and disassembly of a raw material, and is superfluous O2. ** it does not supply, it is completely O2. Fullerene can be compounded without supplying. For this reason, it is very effective as an extensive manufacturing method of fullerene.
[0037] By this invention approach, since the system of reaction, the cooling system, and the recovery system are arranged toward the bottom from the top in this order, while a product flows to a recovery system smoothly and the yield of fullerene improves, continuous running becomes easy.
[0038]
[Example]
Example 1 Fig. 1 is drawing of longitudinal section showing the example of the manufacturing installation of fullerene. This equipment is a manufacturing installation of the fullerene of a vertical mold, and the plasma generating system 7 is formed downward in the upper limit part of the tubed plasma producer 35 which made the direction of a cylinder axis the vertical direction. This example has shown the plasma gun which generates DC arc discharge plasma jet as an example of a plasma generating system.
[0039] Connecting piping 36 is connected to the lower part of this plasma producer 35, and this connecting piping 36 is inserted into the product collection tank 37. The bulb 38 is formed in the lower limit of the product collection tank 37. The bag filter 40 is connected to the side face of the product collection tank 37 through piping 39, and this bag filter 40 is having that interior decompressed by the vacuum pump 19. In addition, said plasma producer 35 and connecting piping 36 have cooling wall (signs A, B, and C) structure.
[0040] Thus, in the equipment of constituted Fig. 1, constant feeding of the raw material is

continuously carried out to the thermal plasma 11 generated downward from the plasma generating system 7, and the soot-like product which reacts into thermal plasma 11 and contains fullerene generates. This product is introduced into the product collection tank 37 from connecting piping 36, and that most deposits it in this product collection tank 37. The products which were not deposited are completely collected in a bag filter 40.

[0041] Since according to the manufacture approach of fullerene using the equipment shown in this Fig. 1 the plasma producer 35 is formed in the vertical direction and thermal plasma 11 is also injected downward, the soot-like product containing the generated fullerene falls the inside of the plasma producer 35 efficiently, and is introduced into the product collection tank 37. For this reason, there is little deposition of the product in the plasma producer 35, and it can carry out continuous running over a long time. Moreover, since the soot-like product containing fullerene is recovered nearly completely by the product collection tank 37 and the bag filter 40, its recovery of fullerene is also very high.

[0042] In addition, you may be either although both the collection tank 37 and the bag filter 40 are used in Fig. 1. Moreover, although the plasma producer 35 is formed in the direction of a vertical in the example of Fig. 1, it is good also as slanting facing down.

[0043] Moreover, if the product (fullerene may be mixing) which adheres in the plasma producer 35 and connecting piping 36 is written at any time by the sweeper made from heat-resisting material, the generation effectiveness of fullerene will improve further. Moreover, in a bag filter 40, if the product which adheres by excitation is desorbed at any time, operation of long duration will be attained more.

[0044] In the equipment of Fig. 1, liquid benzene was supplied from the feeding system at the rate of 3ml / min as a raw material by making helium into associated gas (the flow rate of 2l. / min). The preheating of this benzene is carried out to 80 degrees C with a heater type preheater, and it is evaporated and is sent to about 2cm lower stream of a river of the plasma generating system 7 in the condition of having been kept warm as it is.

[0045] As plasma gas, Ar was supplied by min and 20l. / helium was supplied at a rate of 20l. / min (all flow rates are converted above at the time of ordinary temperature ordinary pressure).

[0046] The other main conditions are as follows.

[0047] Plasma generating system power 25-40kW (water-cooled ****** of a plasma generating system)

Reaction section internal pressure 55Torr reaction sections temperature Outlet gas temperature of 1200 - 1500K bag filter 40 In early stages, it is 50 degrees C. Then, it goes up gradually to 80 degrees C.

Charge residence time of plasma jet Uchihara It was recovered by the bag filter 40 while about 50g (** C60 and C70) of soot-like matter adhered to the collection tank inside in the feeding of about 1ms, consequently 30min. When the adhesion product of this collection tank inside was raked out, it combined with the recovery object of a bag filter 40 and the toluene extract was carried out, the diethylether insoluble element of them (fullerene C60+C70) was about 0.4g in the trial at the time of the most numerous.

[0048] Moreover, only about 1g soot-like product adhered in the plasma producer 35, and it was admitted that cooling effectiveness hardly fell.

[0049] The ultraviolet-visible absorption spectrum in the toluene solvent of this insoluble element is shown in Fig. 2. It turns out that the spectrum of this insoluble element has a gently-sloping peak near 460-480nm again, and has become about a peak or the shoulder at the sum of the spectrum of C60 and C70 of the standard sample of reference data at 314nm, 334nm, 363nm, 381nm, and 407nm.

[0050] Moreover, the electron impact ionization mass spectrum of this insoluble element is shown in Fig. 3. The peak of 720, 360 (C60), and 840 and 420 (C70) equivalent to the mass number/charge of univalent [of C60 and C70 / each] and a divalent cation is seen. From these, it was checked that fullerene C60 and C70 had been compounded.

[0051] In addition, for the comparison, piping 39 and a bag filter 40 were removed among the equipment of Fig. 1, it reconstructed so that it might be made to exhaust with the direct

vacuum pump 19 from a collection tank 37, and it operated on the same conditions using the equipment which installed from the plasma generating system 7 (plasma gun) to the collection tank 37 further so that it might fall sideways (condition rotated 90 degrees).
[0052] Consequently, about 30g of soot-like products was collected from the inside of a collection tank 37 and the plasma producer 35, and they became less than the result of an example 1. Moreover, about 13g adhered to a part for the cooling wall in the plasma producer 35 among products, and it was presumed that cooling effectiveness was falling.
[0053]
[Effect of the Invention] According to the manufacture approach of the fullerene of this invention the above passage, moreover, it is superfluous O2, carrying out continuation supply of the raw material. ** it does not supply, it is completely O2. Fullerene can be compounded without supplying. Therefore, it is possible for it to be stabilized, to be able to manufacture fullerene, to continue moreover at a long period of time, and to carry out continuation manufacture.
[0054] Furthermore, since a product is efficiently transported to the stripping section prepared caudad and it can collect, the yield of fullerene improves and it becomes easy to carry out continuous running.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is drawing of longitudinal section of a fullerene manufacturing installation used for the example approach of this invention.
[Drawing 2] It is as a result of [of the generation fullerene in the example of this invention] analysis (ultraviolet-visible absorption spectrum of a toluene solution).
[Drawing 3] It is as a result of [of the generation fullerene in the example of this invention / another] analysis (electron impact ionization mass spectrum).
[Description of Notations]
7 Plasma Generating System
19 Vacuum Pump
35 Plasma Producer
37 Product Collection Tank
40 Bag Filter

[Translation done.]

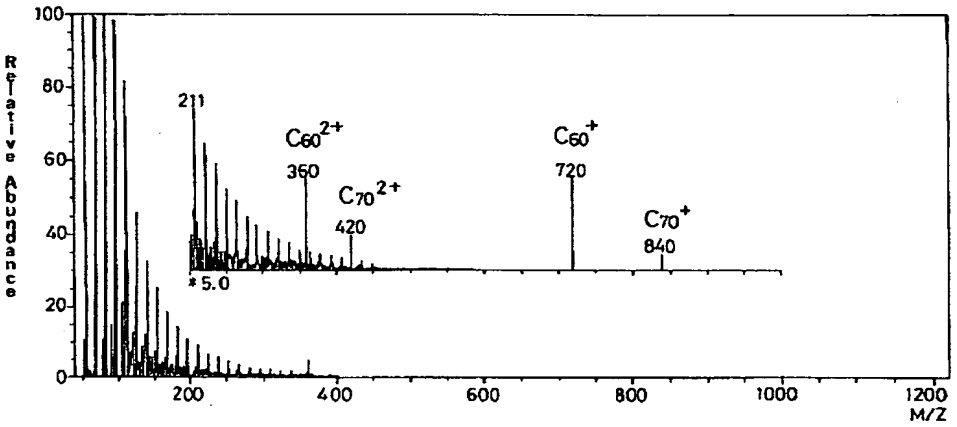
* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DRAWINGS

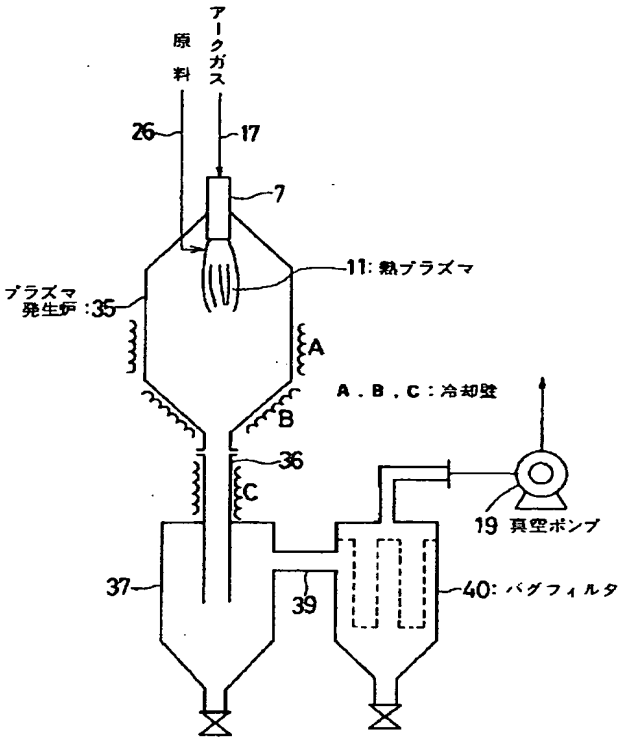
[Drawing 3]

第 3 図



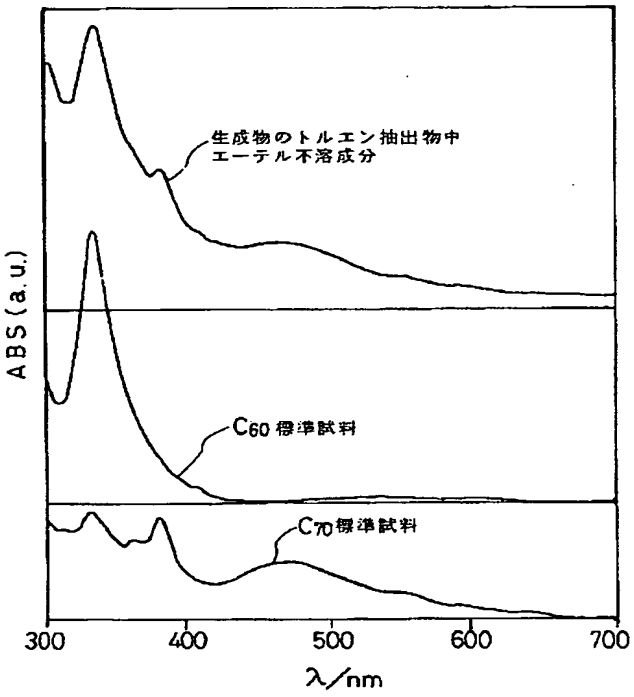
[Drawing 1]

第 1 図



[Drawing 2]

第 2 図



[Translation done.]